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Thermoreversible swelling behaviour of hydrogels based on *N*-isopropylacrylamide with sodium acrylate and sodium methacrylate

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Abstract

Hydrogels were prepared by free radical polymerization in aqueous solution of *N*-isopropylacrylamide (NIPA) and of NIPA with sodium acrylate (SA) and sodium methacrylate (SMA) as comonomers. For each copolymerization three different compositions were used and for all systems three concentrations of a tetrafunctional crosslinker were employed.

Swelling ratios, r = (mass hydrogel/mass dry polymer), were measured on heating from 20°C and then on cooling back to 20°C, and the swelling/deswelling was shown to be thermoreversible. Lower critical swelling temperatures (T_c) were exhibited in copolymers with low concentration of sodium salt. The type of comonomer did not affect the swelling–deswelling behaviour in hydrogels with low concentration of comonomer, but there were strong differences at higher concentrations. These variations were attributed to small differences in the degree of hydrolysis of the SA and SMA units within the hydrogel.

Keywords: *N*-isopropylacrylamide; Sodium acrylate; Sodium methacrylate

1. Introduction

According to the acid-base equilibrium for a weak acid, the degree of dissociation of the acid depends directly on the pH of the medium. The acid will be virtually non-dissociated in a solution buffered at low pH and, on the contrary, the acidic groups will be almost completely ionised in a basic medium. When the acidic units are part of a hydrogel, their degree of ionisation should influence the swelling behaviour of the hydrogel owing to variations in the density of negative charges within the network of the hydrogel. Taking the degree of swelling at neutral pH as a reference, a higher degree of swelling should be expected in a basic medium as a consequence of the repulsive interactions between the negatively charged acidic groups. In contrast, a reduction on the degree of swelling would be normal in a swelling medium buffered at acidic pH resulting from the lack of those repulsive interactions.

In previous work [1] we have studied the swelling behaviour in water at pH = 5.7 of hydrogels based on copolymers of *N*-isopropylacrylamide (NIPA) with the weak acids acrylic acid (AA) and methacrylic acid (MAA). Subsequently [2] the results were extended by examining the swelling–deswelling behaviour at the extrema of pH. The results at pH = 1 were in accordance with those expected considering the acid–base equilibrium of a weak acid under these conditions viz. the degree of swelling was lower than that at neutral pH (although there are some side effects like hydrogen bonding between the components of the hydrogel). Despite the repulsive interactions that exist between the carboxylates groups of the acidic units at pH = 12, the values of the degree of swelling were extremely low. It was concluded that the added NaOH (used to adjust the pH of the water) behaves as an added salt, which screens ionic interactions, so that the gel behaves as if it were uncharged [3].

In order to avoid the interference of external sodium ions at pH = 12, it was considered useful to synthesize copolymeric hydrogels of NIPA with the sodium salts of the AA and MAA, sodium acrylate (SA) and sodium methacrylate (SMA). These two salts are strong electrolytes and are completely ionised in water. Hence, their incorporation as copolymer components has the added advantage of enhancing the level of swelling.

2. Experimental

2.1. Materials

NIPA, the crosslinker *N*,*N*-methylene bisacrylamide (BIS), the activator *N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine

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(TEMED), AA and MAA were purchased from Aldrich Chemical Co. Ammonium persulphate (APS) was obtained from Wilkinson–Vickers Ltd. NIPA was recrystallised from toluene/*n*-hexane (27/73 vol./vol.). AA and MAA were purified by vacuum distillation. All other chemicals were used as received. Deionised water from a Millipore Milli-U10 water purification system was used in the preparation of hydrogels and in the swelling experiments.

SA and SMA were synthesised by neutralising the corresponding acid, AA or MAA, with a methanolic solution of NaOH at 20°C according to the procedure of Morawetz and Rubin [4]. The monomers were filtered, washed with acetone, dried at room temperature and finally dried to constant weight at 40°C in a vacuum oven. This procedure had already been demonstrated previously [5] to afford high yield and purity.

2.2. Synthesis of hydrogels

Gels were prepared by free radical crosslinking copolymerization in water, which is a solvent for all components of the feed mixture. The ratio NIPA/water was fixed at 15/85 (wt/wt) in all cases and the overall concentrations of initiator (APS) and activator (TEMED) were each 1 mol% with respect to total monomers. To a known mass of solid principal monomer (NIPA) in a tube were added appropriate volumes of aqueous solutions of APS, BIS and sodium salt comonomer of known concentrations. After dissolution of the NIPA the resultant solution was degassed with nitrogen for 10 min. During this degassing the tube was immersed in an ice/water bath to minimise the slight possibility of any pre-polymerization. For the same precautionary reason addition of the solution of activator to the feed mixture was made only at the final stage, i.e. just prior to filling the moulds formed by the glass microscope slides separated by a 50 × 10 mm poly(tetrafluoroethylene) gasket of 2 mm thickness. The approximate volume of feed mixture is thus $(50 \times 10 \times 2) \times 10^{-3} = 1$ cm^3 of which ca. 0.85 cm^3 is water and the remainder comprises the monomers and crosslinker. It was not necessary to record the mass of feed mixture in the mould (*vide infra*). The moulds were placed in sealed plastic bags, which were immersed in a water thermostat. The copolymerizations were found to be slower than the corresponding ones in which the comonomers were in the acid form. Consequently, here they were conducted at 30°C for 24 h (instead of at 24°C for 6 h).

After the copolymerization the entire resultant swollen gel was removed from the mould and weighed. As the mass fractions of all components of initial feed mixture were known, the weight of swollen gel allowed the mass of monomers initially in the mould to be calculated. The swollen gel was washed thoroughly several times with de-ionised water and dried successively at room temperature, then at 45°C and finally to a constant weight in a vacuum oven at 45°C. The xerogel obtained was weighed. The ratio of this weight to that of total monomers initially indicated a very high conversion on a weight basis, $C(C \geq 0.96)$ Since the extracted dry gel is crosslinked polymer the value of C is, in principle, only an apparent one that does not allow for possible conversion of monomers to soluble linear copolymer. We have not attempted to distinguish between the latter and unreacted monomers in the washings. However, allowance for any linear copolymer could give an actual fractional conversion that is greater than the apparent one and the sol fraction removed must be ≤ 0.04. Hence, the overall average copolymer composition can be approximated very well to the initial feed composition.

2.3. Swelling measurements

Each dried sample in the form of a thin strip (ca. 0.1 g) was immersed at room temperature in a large excess of water (ca. 100 cm^3) in a poly(propylene) jar fitted with a poly(propylene) screw cap. It was confirmed that a period of 24 h was more than adequate to ensure attainment of swelling equilibrium. The samples were then brought to each of several increasing temperatures T (the lowest of which was generally 20°C) and held thereat for 6 h to attain equilibrium. Determination of the gravimetric swelling ratio r via Eq. (1), in which w_h and w_x the weights of swollen and dry strips respectively, is a procedure that demands great care and attention to detail in order to obtain accurate and reproducible results.

$$r = \frac{w_h}{w_x}. \tag{1}$$

Essentially, at any temperature the removed swollen strip was surface dried lightly and rapidly and weighed (w_h) in a stoppered tared vial. After replacement in water for a minimum of 30 min, determination of w_h was made as before. This procedure was repeated at least three more times and an average value of w_h was used to calculate r. The uncertainty or error in r was taken to arise solely from that in w_h, which was $= 0.5\%$ with respect to the average value of w_h. After measurements at the highest temperature (generally 60°C but also > 60°C for several systems), the same procedure was adopted at each of several decreasing temperatures. The xerogel had previously been subjected to a rigorous washing process and indeed the absence of any sol fraction was confirmed by deliberately drying to completeness and weighing the samples after swelling/deswelling over the whole range of T. The final weight was identical in value to w_x This finding also confirms that it was not necessary to have changed or replenished the water during the swelling/deswelling.

A microprocessor pH meter RE357Tx (EDT Instruments) affording a precision of 0.02 pH unit gave a value of 5.7 for the pH of the swelling medium at room temperature. Specific effects noted elsewhere, [2] resulting from the dissolved HCl or NaOH do not apply here to the present investigation in which the swelling medium was pure water. Moreover, although pH can be controlled by the use of buffers (e.g.

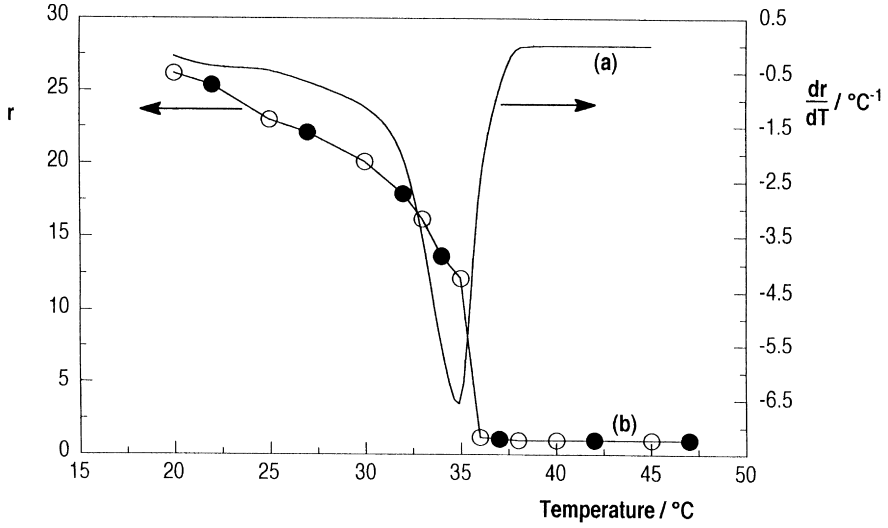


Fig. 1. Influence of temperature on swelling ratio r for hydrogel of NIPA/SMA1/BIS0.5. (a) Differential plot of dr/dT T vs T (b) Data obtained on heating (○) and on cooling (●).

citrate–phosphate [6]) it should be noted that: (a) even with a buffer of fixed composition a small change in pH with T is possible because of the temperature dependence of the dissociation constant K_a of the acid component; and (b) the presence of dissolved salts even at low concentration can have a dramatic effect on swellability in certain circumstances [7]. The pH of the water was measured only at the start, i.e. at room temperature and not checked or adjusted by buffer thereafter. However, application of the integrated van't Hoff equation to tabulated values [8] of the ionic product for water K_w at various temperatures indicated that the calculated value of pH changed by a rather small amount (ca. 0.6 pH unit) over the total range used for swelling/deswelling. As is customary in such work, no stirring or agitation was considered necessary during the swelling because of (a) thinness of the strips coupled with long equilibration time and (b) the risk of damaging the strips, which were rather fragile at high values of r.

3. Nomenclature

The samples are denoted by abbreviations for components together with their compositions, that of a sodium salt comonomer being its mol% with respect to NIPA and that of BIS being its mol % with respect to total monomers. For example, a hydrogel: NIPA/SA1/BIS0.25 is synthesised from a feed solution that contains 85 g of water and 15 g of NIPA (≡15/113.2 mol NIPA). The content of SA is (1/100)(15/113.2) mol and the content of BIS is (0.25/100)[(15/113.2) + (1/100) (15/113.2)] mol.

4. Results and discussion

The swelling behaviour of poly (NIPA), poly(NIPA-co-AA) and poly(NIPA-co-MAA) has been described in detail previously [1,2]. During the discussion of the present findings we will use those already known results in order to compare them with the new data obtained for the hydrogels of poly(NIPA-co-SA) and poly(NIPA-co-SMA).

The contents of sodium salt comonomers were 1, 5 and 10 mol% and for each of the systems the contents of BIS were 0.25, 0.5 and 1 mol %. For all of these $2 \times 9 = 18$ copolymers r was measured at a minimum of 10 different temperatures starting from 20°C. The selected temperatures were separated by ca. 5°C except in the vicinity of the lower critical swelling temperature (T_c), where they were separated by ca. 1°C. As the deswelling is not discontinuous, it is not easy to assign an exact value to T_c. Hence we have used a computer program to afford the derivative dr/dT at each temperature. As can be seen in Fig. 1(a) the critical temperature is indicated clearly at the minimum of the curve. The swelling experiments were performed in a similar way, measuring the degree of swelling at several decreasing temperatures. In an example of the relevant plot (Fig. 1(b)) it is seen that the experimental points corresponding to the deswelling process and those obtained on cooling the sample are in excellent agreement and hence it is verified that the swelling–deswelling transition is thermoreversible.

The profile of the deswelling curves depends on the composition of the hydrogel and will be discussed later. Deswelling is complete ($r = 1$) at high temperatures except for the hydrogels NIPA/SMA5/BIS0.25 and NIPA/SMA10/BIS0.25. The highest degree of swelling measured (i.e. that at 20°C) increases as the concentration of comonomer increases. This increase is a consequence of the ionic osmotic pressure owing to the increasing content of negatively charged carboxyl groups. All systems exhibit the customary decrease in r with increasing content of BIS.

Table 1
Swelling ratio at, below and above the critical temperature for poly(NIPA-co-SA) hydrogels

NIPA/SA1/BIS0.25		NIPA/SA1/BIS0.5		NIPA/SA1/BIS1	
T/°C	*r*	*T*/°C	*r*	*T*/°C	*r*
20	41.5	20	29.3	20	18.4
35[a]	19.7	35[a]	8.1	35[a]	6.8
45	1.0	45	1.0	45	1.0
NIPA/SA5/BIS0.25		NIPA/SA5/BIS0.5		NIPA/SA5/BIS1	
20	139	20	68.0	20	40.1
43[a]	71.1	45	20.1	45	14.8
52	1.0	52	1.0	52	1.0
NIPA/SA10/BIS0.25		NIPA/SA10/BIS0.5		NIPA/SA10/BIS1	
20	399	20	117	20	79.3
59[a]	210	60	32.8	60	38.0
75	1.1	75	1.0	75	1.0

[a] Critical temperature.

4.1. Concentrations of SA and SMA = 1 mol % with respect to NIPA

Poly(NIPA-co-SA) and poly(NIPA-co-SMA) hydrogels exhibit the same thermosensitive behaviour. The values of T_c and the degree of swelling at selected temperatures are shown in Tables 1 and 2. The value of the critical temperature is 35°C for every hydrogel, independent of the concentration of BIS. The nature of the swelling–deswelling transition is not very clear, since some authors have described a discontinuous transition [3,9] but similar systems have been reported to exhibit a continuous one [3,6]. As can be seen in Fig. 1, the variation of the degree of swelling with temperature is a continuous process.

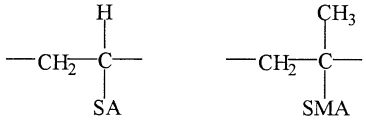
At comonomer contents > 1 mol% (see Section 4.2) the process is markedly more continuous. This sequence of findings suggests that discontinuity might be exhibited at very low content of comonomer. Hence, to assess this possibility, additional samples having contents of SA and SMA of 0.1 mol% were prepared and the phase diagrams of the swelling–deswelling were established in the normal manner. The variation of the degree of swelling with temperature was of a continuous form even in these systems. Consequently, the general disaccord regarding the form of the transition remains unresolved. Possible factors may be related to (a) the dimensions of the hydrogel (most of the authors, who reported a discontinuous transition, used capillary samples [3,9–12] or submicron gel beads [13]) and/or (b) the rate of heating/cooling and/or (c) the stabilisation time between measurements at two different temperatures. No details regarding (b) and (c) were provided in the relevant papers.

4.2. Concentrations of SA and SMA = 5 or 10 mol% with respect to NIPA

With one exception, the highest degree of swelling measured is greater for hydrogels of poly(NIPA-co-SMA) than for those of poly(NIPA-co-SA) (see Tables 1 and 2). This behaviour can be explained on the basis of hydrolysis equilibrium. Salts of weak acids are decomposed by water with formation of free acid and free base:

$$-\mathrm{RCOONa} + \mathrm{H_2O} \rightleftharpoons -\mathrm{RCOOH} + \mathrm{NaOH} \quad (2)$$

where R is:



The process of hydrolysis is reversible. As the salt is practically completely ionised and the base is strong, Eq. (2) can be written:

$$-\mathrm{RCOO^-} + \mathrm{H_2O} \rightleftharpoons -\mathrm{RCOOH} + \mathrm{OH^-} \quad (3)$$

and therefore,

$$K_h = \frac{[\mathrm{OH^-}][-\mathrm{RCOOH}]}{[-\mathrm{RCOO^-}]} \quad (4)$$

Since the base is strong, $[\mathrm{OH^-}]$ is practically equal to

Table 2
Swelling ratio at, below and above the critical temperature for poly(NIPA-co-SMA) hydrogels

NIPA/SMA1/BIS0.25		NIPA/SMA1/BIS0.5		NIPA/SMA1/BIS1	
T/°C	*r*	*T*/°C	*r*	*T*/°C	*r*
20	40.2	20	26.2	20	18.3
35[a]	16.1	35[a]	12.2	35[a]	7.7
45	1.0	45	1.0	45	1.0
NIPA/SMA5/BIS0.25		NIPA/SMA5/BIS0.5		NIPA/SMA5/BIS1	
20	183	20	122	20	73.9
62[a]	114	45	68.5	45	32.8
80	42.1	70	1.0	70	1.0
NIPA/SMA10/BIS0.25		NIPA/SMA10/BIS0.5		NIPA/SMA10/BIS1	
20	309	20	143	20	108
65[a]	182	65	36.3	50	39.4
85	55.1	75	1.1	70	1.0

[a] Critical temperature.

Table 3
Values of c and calculated values of $[OH^-]$, pH and α for poly(NIPA-co-SA) hydrogels at 20°C

Hydrogel	c/mol l^{-1} × 10^3	$[OH^-]$/mol l^{-1} × 10^5	pH	α
NIPA/SA1/BIS0.25	2.17	2.94	9.47	73.9
NIPA/SA1/BIS0.5	3.10	3.51	9.55	88.2
NIPA/SA1/BIS1	5.05	4.48	9.65	113
NIPA/SA5/BIS0.25	3.08	3.50	9.54	87.9
NIPA/SA5/BIS0.5	6.34	5.02	9.70	126
NIPA/SA5/BIS1	10.9	6.57	9.82	165
NIPA/SA10/BIS0.25	2.05	2.86	9.45	71.8
NIPA/SA10/BIS0.5	7.04	5.29	9.72	133
NIPA/SA10/BIS1	10.4	6.44	9.81	162

[base], and because the salt is assumed to be completely ionised, $[-RCOO^-]$ is practically equal to [salt]. Hence Eq. (4) can be written as:

$$K_h = \frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]} \tag{5}$$

where K_h is the hydrolysis constant.

In the solution there are two equilibria holding simultaneously

$$-RCOOH \rightleftharpoons -RCOO^- + H^+$$

$$K_a = \frac{[H^+][-RCOO^-]}{[-RCOOH]} \tag{6}$$

$$H_2 \rightleftharpoons OH^- + H^+$$

$$K_w = [H^+][OH^-] \tag{7}$$

Combination of Eqs. (6) and (7) with Eq. (4) yields:

$$K_h = \frac{K_w}{K_a}. \tag{8}$$

If c is the total salt concentration in mol l^{-1}, then as $[-RCOOH] = [OH^-]$:

$$\frac{[-RCOOH][OH^-]}{[-RCOO^-]} = K_h = \frac{[OH^-]^2}{c}. \tag{9}$$

Therefore from Eq. (8):

$$\frac{[OH^-]^2}{c} = \frac{K_w}{K_a}, \tag{10}$$

$$[OH^-] = \sqrt{\frac{cK_w}{K_a}}. \tag{11}$$

It is known that the values of the pK_a for the PAA and PMAA are 6.4 and 6.9, respectively [14,15], under the experimental conditions used in this work (T = 20°C and pH = 5.7). The value of the concentration c has been taken as the number of moles of either SA or SMA in the hydrogel divided by the volume of water absorbed by the hydrogel. Therefore, $[OH^-]$ can be calculated according to Eq. (11). As the equilibrium takes place within the hydrogel, the $[OH^-]$ calculated in this way only applies to the hydrogel itself, the pH of the swelling medium being virtually unaffected. The pH inside the hydrogel can be calculated according to Eq. (7):

$$-\log[H^+] = \text{pH} = \log[OH^-] - \log K_w. \tag{12}$$

Finally, the ratio α between the concentration of unhydrolysed salt $[-RCOO^-]$ and that of the hydrolysed one $[-RCOOH]$ can be calculated from Eq. (13):

$$\alpha = \frac{[-RCOO^-]}{[-RCOOH]} \approx \frac{c}{[OH^-]}. \tag{13}$$

In Eq. (13) the approximation of $[-RCOO^-]$ to c is valid

Table 4
c and calculated values of $[OH^-]$, pH and α for poly(NIPA-co-SMA) hydrogels at 20°C

Hydrogel	c/mol l^{-1} × 10^3	$[OH^-]$/mol l^{-1} × 10^5	pH	α
NIPA/SMA1/BIS0.25	2.24	1.68	9.22	133
NIPA/SMA1/BIS0.5	3.48	2.09	9.32	166
NIPA/SMA1/BIS1	5.07	2.53	9.40	201
NIPA/SMA5/BIS0.25	2.32	1.71	9.23	136
NIPA/SMA5/BIS0.5	3.48	2.09	9.32	166
NIPA/SMA5/BIS1	5.79	2.70	9.43	215
NIPA/SMA10/BIS0.25	2.62	1.82	9.26	145
NIPA/SMA10/BIS0.5	5.68	2.67	9.43	212
NIPA/SMA10/BIS1	7.57	3.09	9.49	246

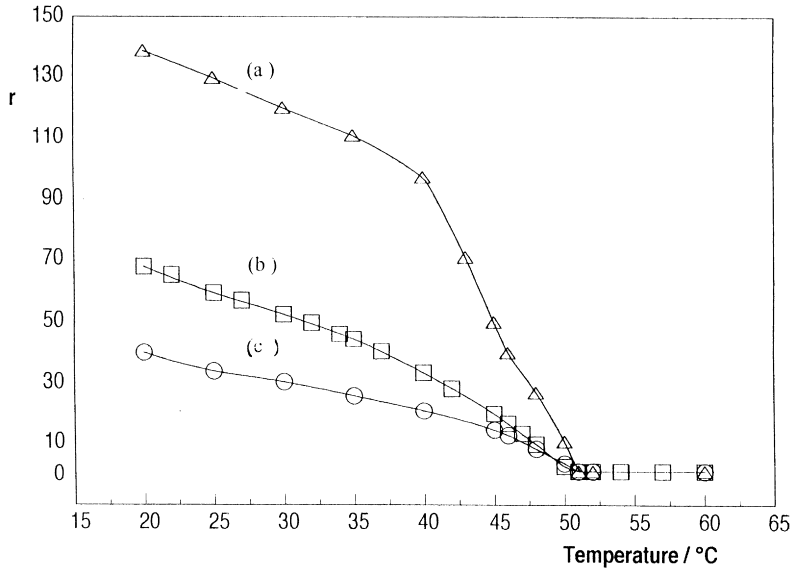


Fig. 2. Variation of swelling ratio r with temperature for hydrogels of (a) NIPA/SA5/BIS0.25, (b) NIPA/SA5/BIS0.5, (c) NIPA/SA5/BIS1.

since the values of $[OH^-]/c$ are of the order of 10^{-2} The smaller the value of α the higher the degree of hydrolysis.

For hydrogels containing either SA or SMA the extent of hydrolysis, as indicated by the values of $[OH^-]$ and pH, increases with content of sodium salt comonomer in xerogel. Increasing the content of BIS decreases the swellability and hence increases the concentration, c, of sodium salt comonomer in the hydrogel. The effect is again an increase in hydrolysis.

Within the swollen hydrogel the concentration of SA and SMA units is c, the concentration of OH^- groups produced by hydrolysis is $[OH^-]$ and the level of acidity is pH. The values of these as well as the ratios α are summarised in Tables 3 and 4, which show that, for a similar concentration of comonomer, the degree of hydrolysis of the SA units is always bigger than that found in the hydrogels containing SMA. This means that the density of negative charges and therefore the ionic osmotic pressure is higher in poly(NIPA-co-SMA) than in poly (NIPA-co-SA) hydrogels. Hence, the higher degree of swelling found in poly (NIPA-co-SMA) hydrogels can be attributed to this factor. The effect is negligible at low concentration of comonomer (1 mol%) but it is quite important at higher concentrations (5–10 mol%).

None of the discussion above takes into account the possible influence of the effective crosslinking density ν_e of the xerogel (as opposed to the nominal value calculated from the molar concentration of BIS in the feed mixture). It could happen that the observed differences among swelling

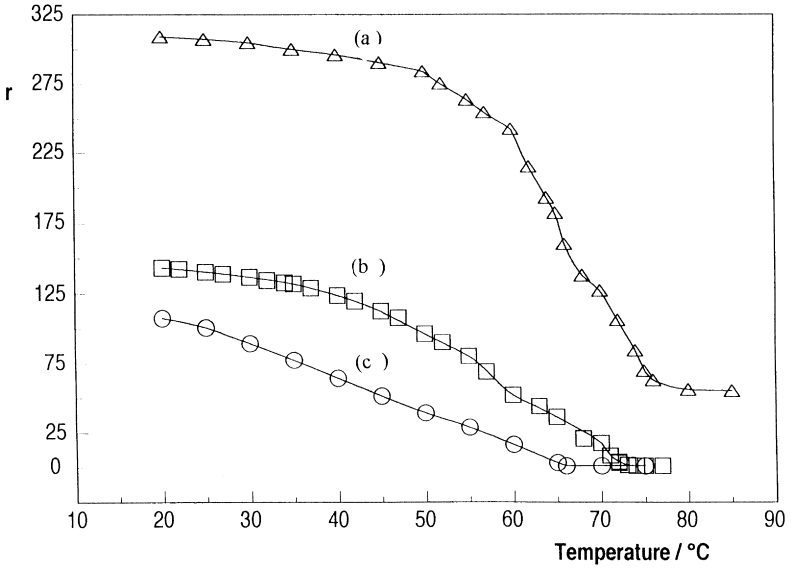


Fig. 3. Variation of swelling ratio r with temperature for hydrogels of (a) NIPA/SMA10/BIS0.25, (b) NIPA/SMA10/BIS0.5, (c) NIPA/SMA10/BIS1.

data might arise, at least in part, from differences among values of ν_e Compression–strain measurements were made on hydrogels of NIPA/SA5/BIS1 and NIPA/SMA5/BIS1. As a result of the presence of a diluent, water, in the crosslinking polymerization process, a correction factor involving the ratio of volume of dry unstrained xerogel to volume of network at formation had to be applied [16,17]. The resultant value of ν_e was virtually the same for both samples (0.027 mol dm^{-3} for NIPA/SA5/BIS1 and 0.026 mol dm^{-3} for NIPA/SMA5/BIS1) at all temperatures. Hence, the higher swellability of hydrogels containing SMA can be attributed at least in part to the greater degree of hydrolysis of the SA units within the hydrogel.

The profile of the deswelling curves is very similar for poly(NIPA-co-SA) and for poly(NIPA-co-SMA) hydrogels. Figs. 2 and 3 show typical plots of the phase diagrams for both type of hydrogels. As can be seen in these figures, the deswelling is a continuous process and it is impossible to determine a single T_c in hydrogels with high and medium content of BIS. Similar behaviour was observed in hydrogels of strong polyelectrolytes like poly(NIPA-co-2-methyl-2-acrylamido-propanesulphonic acid) [1] and in hydrogels of poly(NIPA-co-AA) and poly (NIPA-co-MAA) swollen at pH = 12 (conditions at which the carboxylic groups are completely ionised) [2]. In the present systems the critical transition becomes clearer at low concentration of crosslinker but is still very broad, extending over a range of ca. 20°C.

Hydrogels of poly(NIPA-co-SMA) with low concentration of BIS do not reach complete deswelling even at high temperatures (see Table 2 and Fig. 3). According to the results obtained from the hydrolysis equilibrium, the degree of hydrolysis of the SMA units is lower than that of the SA ones and, hence, we can consider that the former is a stronger electrolyte. Therefore, the higher ionic osmotic pressure in the case of poly (NIPA-co-SMA) hydrogels must be the reason for this behaviour [3].

Prior to presentation of general conclusions, attention will be paid to some specific issues not addressed in the text. Fractions of sequences of selected lengths for the comonomer units in copolymers of *N*-vinyl-2-pyrrolidone (VP) with several hydrophobic comonomers have been calculated at several stages of fractional conversion and were shown to have a semi-quantitative bearing on the water uptake in the corresponding hydrogels [18]. For copolymers of a zwitterionic monomer with a neutral comonomer Monte Carlo simulation calculations afforded a distribution of dyads as a function of copolymer composition that provided a useful interpretation of the experimentally observed synergism in swelling of the corresponding crosslinked xerogels in water [19]. A different type of calculation applied to the copolymerization of VP with a neutral comonomer and a tetrafunctional crosslinker allowed the terpolymer compositional drift with conversion to be computed; of especial interest was the demonstrated inhomogeneous crosslinking of the network at high contents of VP [20]. In all these examples a knowledge of the reactivity ratios or, if not available, the *Q*, *e* parameters was an indispensable requirement. The values of such ratios or parameters were not available for the systems investigated here. Even if they had been, quantification of microstructure and/or heterogeneity would only have added to characterisation of the materials. They would have had little or no direct bearing on thermodynamic aspects [21], viz. the main focus of thermoreversibility in swelling. Dynamic light scattering from polymer solutions has been extended to studies on gels, which possess a collective diffusion coefficient and a correlation length [22]. In principle, the distribution of the latter offers an extremely promising approach to quantifying the heterogeneity of crosslinking. Despite development of new theory and production of some experimental results in this laboratory [23], it is evident that, because of several (mainly experimental) constraints and difficulties, it will be some time before the technique can be used on a reliable, routine basis for this purpose.

The finding, that copolymers containing SMA tend to have a higher swellability than the corresponding ones containing SAA, gives rise to the interesting question of why crosslinked poly(SMA) is not preferred to crosslinked poly(SAA) as a superabsorbent material (we are grateful to an anonymous referee for raising this point). The actual materials manufactured are, and seem likely to remain [24], poly (AA-co-SAA). The partial neutralisation can be either before or after the crosslinking polymerization of AA. Economic aspects regarding AA vis-à-vis MAA do not seem to be relevant. If the post polymerization route is adopted, the reason may lie in the relative rates of polymerization of AA and MAA in aqueous solution and/or the relative reactivities of them with the particular crosslinker used. The greater propensities of acrylates cf methacrylates to undergo branching and crosslinking (in the absence of the added crosslinker) may also have some bearing on use of AA. There remains the possibility, of course, that established tradition rather than purely scientific reasons is the underlying reason. As this aspect is subsidiary to the main focus of this article, it seems unprofitable to speculate any further.

5. Conclusions

1. The swelling/deswelling of poly(NIPA-co-SA) and poly(NIPA-co-SMA) hydrogels was found to be thermoreversible.
2. The variation of *r* with temperature is continuous in all the systems studies. T_c is only exhibited in hydrogels with low concentration of sodium salt comonomer.
3. The values of *r* measured here at neutral pH for the present polymers are much larger than those exhibited at any pH for poly(NIPA-co-AA) and poly(NIPA-co-MAA). Therefore, the inclusion of a strong electrolyte in the hydrogel enhances the water absorption.

4. The degree of hydrolysis is higher for the SA than for the SMA units. This fact can explain the higher degree of swelling exhibited by the poly(NIPA-co-SMA) hydrogels with medium to high concentration of comonomer.

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